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Using a Bias Potential in a Constant and Pulse Modes for Structural Engineering Vacuum Arc Nanocrystalline Coatings of Zirconium Nitride

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In order to develop the direction of "structural engineering nitride coatings" in the work conducted systematic analysis of the impact of the negative bias potential (direct and high-voltage pulse) on the structure, substructure and mechanical properties of ZrN coatings obtained by vacuum arc evaporation. Defined boundary value of (– 100 V) DC potential applied to the substrate, below which a high-voltage pulse potential (– 1200 ... – 2000 V quantity that allows to form peaks bias) makes a decisive contribution to the formation of preferred orientation of the crystallites with the [110] axis. The highest values of hardness 43 GPa are achieved at a constant potential -70 V. Supply high-voltage pulse shifts the maximum hardness in the direction of a greater value of the constant potential.

Keywords: Vacuum-arc Deposition method, Mechanical characteristics of coatings, Bias potential, Zirconium nitride.

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1. INTRODUCTION

Zirconium nitride (ZrN) in recent years has attracted increasing interest due to the unique combination of good corrosion resistance, low electrical resistivity, high melting point (about 3263 K) with a sufficiently high mechanical properties and high chemical stability [1-12]. The latter makes it popular as a coating on the blade instrument operating at high speeds.

At a high degree of ionization of the plasma, as in the case of the vacuum-arc method for producing the structure and properties of coatings are largely determined by the bias potential applied to the substrate during deposition [13]. However, in this case, the use of high potentials is limited considerable heating surface during the deposition, resulting in a loss of properties.

For the purpose of reduce the heat in the deposition in the conditions of filing the substrate bias potential, used in the constant potentials less -300V and higher (– 800 ... – 2000 V) submitted in a pulsed mode with a frequency of 7 kHz and the duration of exposure to 10 μs (~ 7 % the total deposition time). It is possible to perform deposition at temperatures below 700 K.

2. MODES OF RECEIVING COATINGS AND METHODS OF RESEARCH

To solve the problem of structural engineering at modernized installation "Bulat-6", equipped with a high-voltage pulse generator which is further supplied to substrate during the deposition process, ZrN coatings were obtained at a pressure of nitrogen atmosphere $P_N = 0{,}65$ Pa, the value of the negative DC bias potential of the substrate supplied to the $U_b = (-27 \ldots -300)$ V and high-voltage pulse potential $U_{ip} = (-0.8 \ldots -2.0)$ kV applied at a frequency of 7 kHz and the duration of exposure to 10 μs. The duration of the deposition process is 1 to 2 hours. Stainless steel plate 12X18H10T 18 × 18 × 2 mm sizes and copper foil used as the substrates.

Micrographs of coatings obtained by raster electron microscope JEOL JSM 840. For the electron microscopy studies of the coating deposited on the copper substrate thickness of 0.2 mm.

Structural studies of the samples were carried out by X-ray diffraction on the "DRON-3M". Radiation Cu-K_α has used in all studies.

Texture parameter was determined by calculation of the pole density P_{hkl} by the method Harris in the direction normal to the sample surface [14]. To calculate P_{hkl} used the relation:

$$P_{hkl} = \frac{w_{hkl}}{\sum w_{hkl}},$$

$$w_{hkl} = \frac{I^{s}_{hkl} / I^{st}_{hkl}}{\sum I^{s}_{hkl} / \sum I^{st}_{hkl}},$$

where I^{s}_{hkl}, I^{st}_{hkl} – the experimentally measured integrated intensities of reflections from planes (hkl) for the investigated coating and non-oriented standard (JCPDS 35-0753); $\sum I^{s}_{hkl}$, $\sum I^{st}_{hkl}$ – total relative intensities of all the reflections of the sample and the standard. To calculate the total integrated intensity was used range of angles $2\theta = 30 \ldots 80°$ in which one gets to reflect all the major planes.

The size of grain-crystallites (regions of coherent scattering) in the nitride film was determined by using a method for approximating the shape of the diffraction curves [15].

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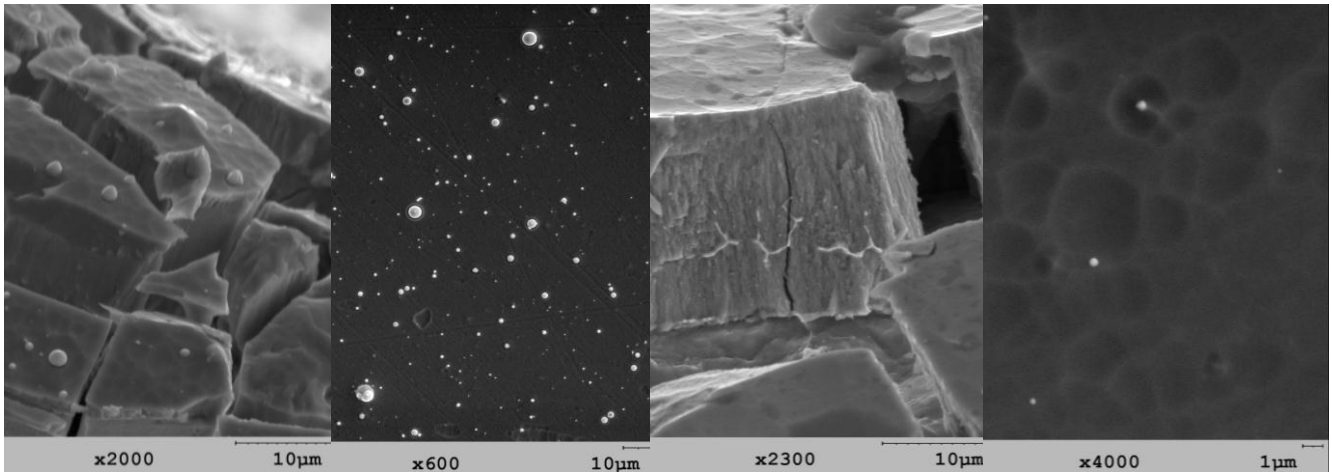

Fig. 1 – The surface morphology and fractographs breaks ZrN coatings (P_N = 0,65 Pa): a, b – U_b = – 40 V; c, d – U_b = – 220 V

The hardness of the samples was determined by using a installing "Micron-gamma" equipped pyramid Berkovich [15] at room temperature (up to a maximum load of 0.5 H).

3. RESULTS AND DISCUSSION

Research of morphology ZrN coatings showed that the coatings produced at a relatively low constant potential bias – 40 V are in the bulk and on the surface of a sufficiently large amount of the droplet phase (see Fig. 1a, b). The structure does not have a expressed by the columnar. Increasing the bias potential leads to a decrease in the droplet phase and the appearance of the columnar structure. In Figure 1c, d shows the surface morphology and fractographs fracture coatings deposited at bias potential supply quantity U_b = – 220 V. Obviously that the coatings are practically no microparticles droplet phase, both in the bulk and on the surface, and the growth structure of coating has a columnar form (see Fig. 1c). This significant reduction of the droplet phase can be explained by the fact that the droplet component, like any other cluster of atoms placed in a plasma acquires a negative (floating) potential and pushes the surface to which a negative potential (in this case the surface of the substrate) [17]. The diffraction spectra of the coatings obtained at different values of U_b without additional high-voltage pulse stimulation are shown in Figure 2. Obviously that over the entire range of bias potentials submitted bias (– 27... –300) V is the formation of a single-phase structural state characteristic of ZrN with a face-centered cubic lattice (structural type NaCl). Thus, depending on the magnitude of the negative bias potential supply varies the ratio of intensities of reflections from different planes, which indicates the appearance of texture (preferred orientation of crystallites). At low bias potential (– 27 ... – 40) V large intensity peak of a (200) indicates the texture [100] axis perpendicular to the plane of growth. A change of texture occurs with the increase in U_b: at U_b = (– 70 ... – 150) V – on bitextural with a preferred orientation of the crystallites with the [311] and [111] perpendicular to the plane of growth, and at U_b exceeding meaningfully – 150 V on nearly uniaxial texture with [111] axis (see. Fig. 2 spectra 6 and 7).

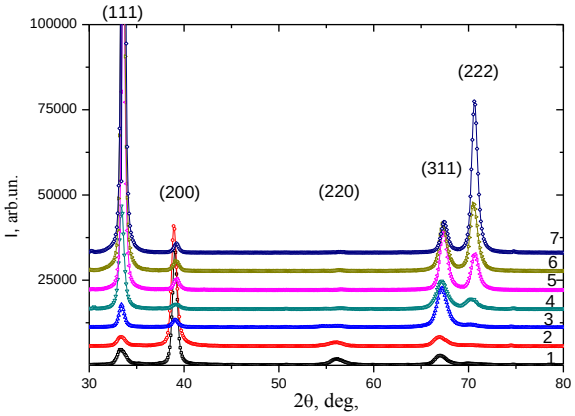

Fig. 2 – Plots X-ray diffraction spectra of coatings ZrN, obtained by P_N = 0,65 Pa, U_{ip} = 0 V, U_b: 1 – – 27 V; 2 – – 40 V; 3 – – 70 V; 4 – – 100 V; 5 – – 150 V; 6 – – 220 V; 7 – – 300 V

When an additional high voltage potential submits to the substrate in the pulsed mode (– 1200 V or – 2000 V) the general trend is observed for the formation of texture [111] for large U_b and significant change in the structural state at smaller U_b (see Fig. 3 and 4). The latter indicates the presence of the boundary energy (potential) in which the definition of the structural state is given by the high-voltage pulsed stimulation, passing with a cascade formation.

Submitting potential U_{ip} = – 1200 V during the entire range of U_b = (– 27 ... – 300) V misses texture [100]. In this case, supply U_{ip} for a small value U_b = (– 27 ... – 70) V stimulates the formation of texture with the [110], which is manifested in increasing reflection from the (220) (see Fig. 3, spectra 1-3). With a larger U_b = (– 70 ... – 100) V as in the case without pulse stimulation formed bitextural state with axes texture [311] and [111], and at U_b = (– 150 ... – 220) V formed in almost uniaxial texture from the [111] axis. However, unlike the formation of coating without impulse stimulation feed U_{ip} = – 1200 V resulted when U_b = – 300 V weaken the relative intensity of (111) (i.e., reducing the degree of texturing axis [111] and the appearance of texture with the [110] (Fig. 3, the spectrum 7).

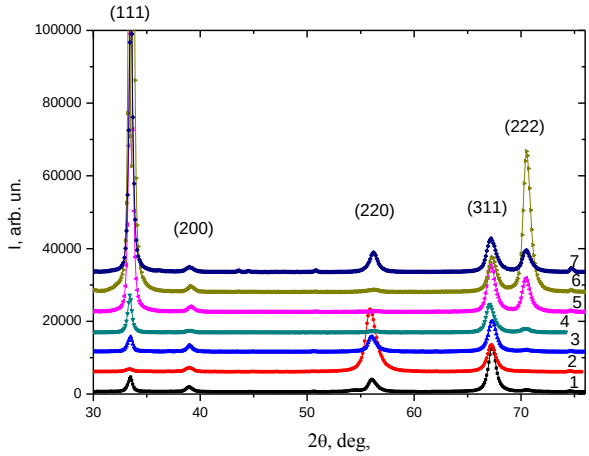

Fig. 3 – Plots X-ray diffraction spectra of coatings ZrN, obtained by P_N = 0,65 Pa, U_{ip} = – 1200 V and U_b: 1 – – 27 V; 2 – – 40 V; 3 – – 70 V; 4 – – 100 V; 5 – – 150 V; 6 – – 220 V; 7 – – 300 V

Submission of the greatest potential U_{ip} = – 2000 V leads to an increase in texture with the [110] at low U_b = (– 27 ... – 70) V in a decrease in the area bitextural state [311] and [111] to U_b = – 100 V at values exceeding which texture formation occurs primarily with the [111]. However, in this case at the maximum U_b = – 300 V new texture appears, in this case with the axis [100] (see. Fig. 4 spectrum 7).

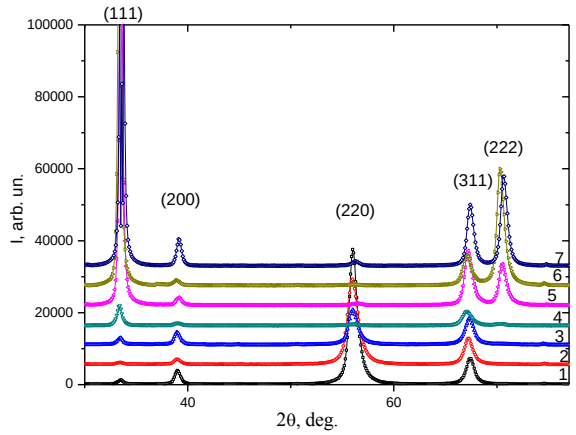

Fig. 4 – Plots X-ray diffraction spectra of coatings ZrN, obtained by P_N = 0,65 Pa, U_{ip} = – 2000 V and U_b: 1 – – 27 V; 2 – – 40 V; 3 – – 70 V; 4 – – 100 V; 5 – – 150 V; 6 – – 220 V; 7 – – 300 V

Thus, the supply of U_{ip} leads to a significant change in the preferential growth of crystallites at low values of U_b. In this case, building texture parameter P_{hkl} for major planes on Harris method [9] are indicative according to U_b for different values of high-voltage pulsed bias potential. Figure 5 shows the corresponding curves for the 4 basic planes (111), (200), (220) and (311).

Obviously that at relatively low constant potential bias (up – 50) V without pulse action occurs the formation of texture with the axis [100]. Increasing capacity to – 100 V leads to a new type of texture with the axis [311]. At higher potentials when determining influence deformation factor - is the formation of texture [111]. The presence of high-voltage pulse potential qualitatively changes the character of texture at a low constant potential bias. With increase in the value of the pulse potential - becomes defining texture [110]. At constant potential exceeding – 100 V high-voltage pulse exposure does not lead to qualitative change in the texture [111]. Thus, there is boundary nature of DC potential at which affects additional high-voltage pulse action.

Considering that calculations showed that the characteristic energy of defect formation by ion implantation from the plasma to form a "thermal spike" is for titanium nitride 500-700 eV [18, 19], when these energies we can expect the emergence of "thermal spikes" and in the case of the isostructural zirconium nitride. As it is known in this case, as the collision energy increases, and with it the radius of the "thermal spike" increases and the time which required for cooling the collision zone to the initial temperature. Then, if the "thermal peak" holds a sufficiently long time, it provides the time needed for significant nuclear relaxation and displacements corresponding to the local annealing. Thus, the high-energy implantation, generating "thermal spikes" with a lifetime greater than the time which required for the stress relaxation forming coating is an effective way to relieve stress during the deposition.

In this case, if the appearance of preferred orientation of [111] is determined by the achievement of a high level of compressive stresses, in particular, by increasing the coating thickness of the nitride coatings [20], then the removal of the stress is the formation of texture [100] as which has the lowest surface energy, or in the implantation of the texture with the axis [110] or [311], which provides minimum radiation damage. Education texture [110] in the case of formation of thermal spikes at constant negative potential – 500 ... – 800 eV system TiZrN confirmed in [21].

On the substructure level of a constant flow without bias potential pulse exposure leads to increase in crystallite size for values less U_b = – 200 V (see Fig. 6). As one of the main causes of this process is to increase the degree of interaction between the nitrogen atoms and the metal, activated by increase in energy. Reducing the size of the crystallites when applying greater capacity may be associated with the process of polygonization under high compressive stresses, reaching apparently critical dislocation movement in the value of ZrN σ = – 6,7 GPa. With this process you can associate the observed decrease in microstrain (1 curve in Fig. 6b).

Feed pulsed high voltage potential reduces microstrain (2 and 3 according to Fig. 6). This increase in the average energy of the particles as a result of pulse stimulation leads to process of polygonization associated with the ordering of dislocation defects, even at fairly low constant potential (about – 100 V).

Feed at constant potential deposition leads to nonmonotonic effect of hardness modification (see Fig. 7, the curve of 1).

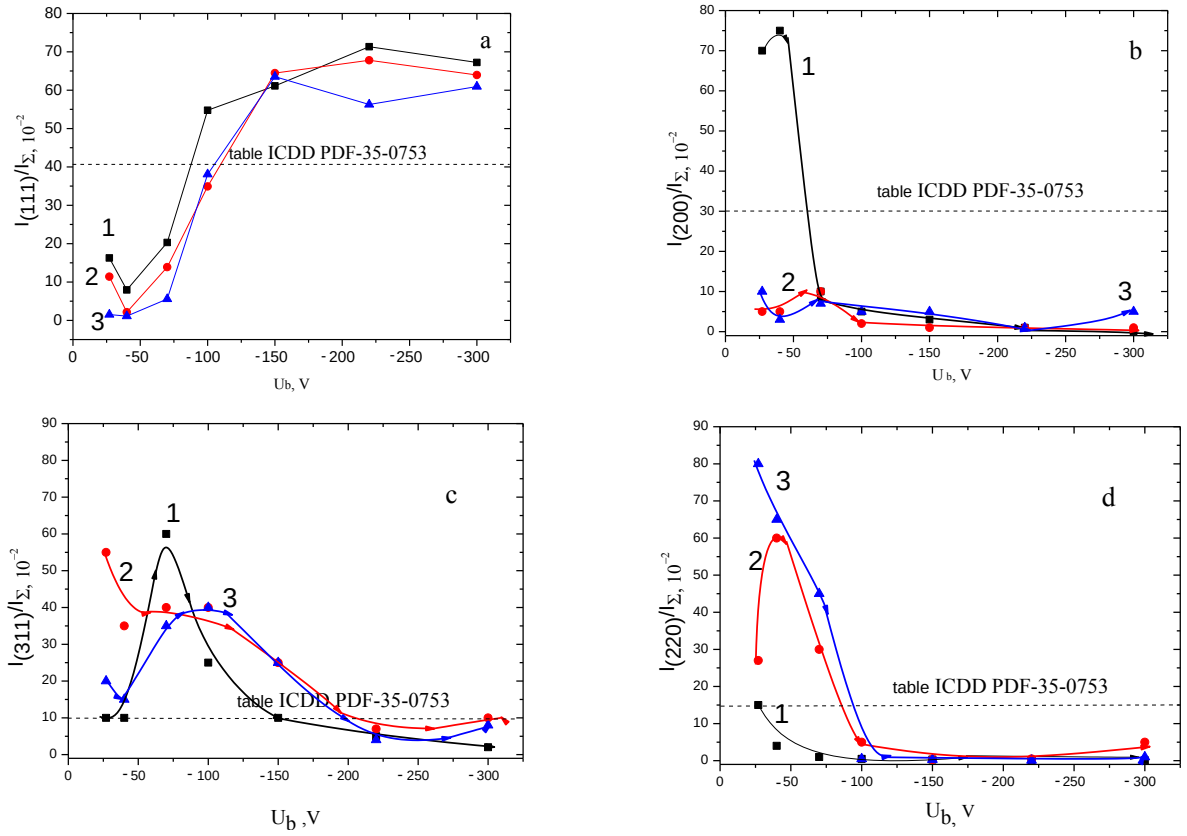

Fig. 5 – Depending on the parameter of texture P_{hkl} from values U_b for different planes: a – (111), b – (200), c – (311), d – (220); 1 – U_{ip} – 0 V, 2 – U_{ip} – 1200 V, 3 – U_{ip} – 2000 V

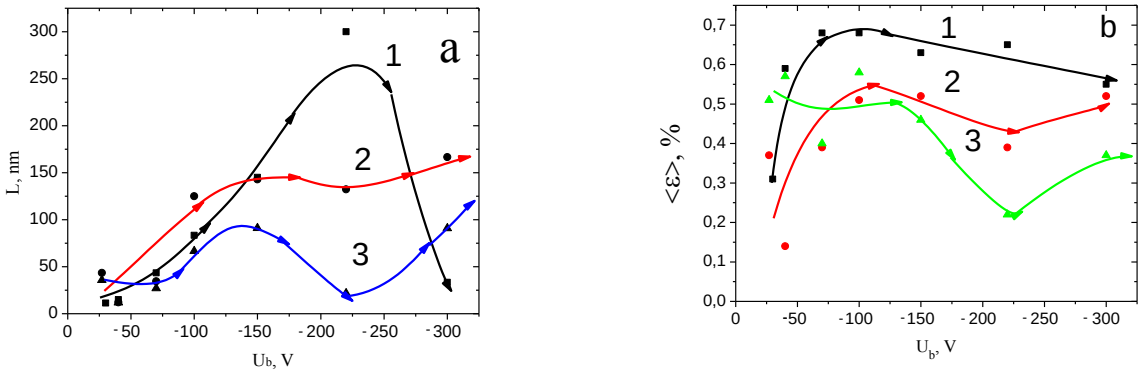

Fig. 6 – The dependence of the crystallite size (a) and microstrain (b) from the constant potential at P_N = 0,65 Pa: 1 – U_{ip} = 0 V; 2 – U_{ip} = – 1200 V; 3 – U_{ip} = – 2000 V

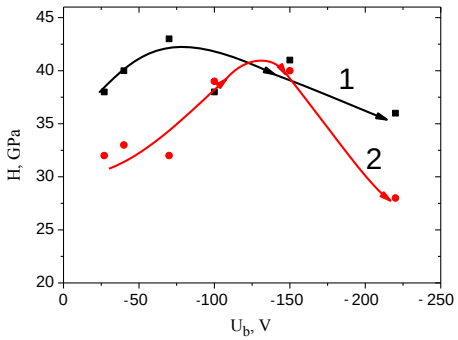

Fig. 7 – Dependence of the microhardness of coatings from values of the constant potential at P_N = 0,65 Pa: 1 – U_{ip} = 0 V, 2 – U_{ip} = – 2000 V

This change consists in the growth hardness to the bias potential – 100 V that may be associated with increase in compressive stress and greater efficiency formation of nitrides. Fall hardness at higher constant potential may be due to increase in structural defects. Submission of pulsed high voltage potential is accompanied by relatively lower hardness at low U_b. However, in the range of – 100 ... – 150 V hardness increases, transferring obtained in this way coating superhard discharge. As can be seen from a comparison with the substructural characteristics – appearance in this interval U_b high hardness with pulse stimulation correlates with decrease in the average crystallite size. Also, as is well known, the impulse high voltage stimulation increases the efficiency of formation of nitrides.

4. SUMMARY

Using negative bias potential (in a direct and high-voltage pulsed modes) the regularity of its influence on the surface morphology of growth, structure, substructure and mechanical properties.

It is established that the effect of the negative potential on the surface morphology during the deposition effect in reducing the droplet phase. This is determined by the acquisition of a drop of the negative charge and the repulsion of its negatively charged surface of the substrate during the deposition.

At the structural level supply potential leads to the formation of preferred orientation of the crystallites. Feed small in magnitude $U_b = (-50$ V) leads to preferred orientation of growth of crystallites with axis [100]. At higher constant potential $U_b = (-50$ ... $-100)$ V texture is formed [311], which at $U_b = (-150$ ... $-300)$ V goes into texture with the axis [111]. Submission of high-voltage pulses results in texture [110] and the formation at high U_b bitextural status with the axises [111] and [110].

On the substructure level in the range of $U_b = (-100$ ... $-250)$ V supply high-voltage pulses results in decrease in the average crystallite size and microstrain relaxation.

The highest values of hardness 43 GPa are achieved at constant potential – 70 V. Supply high-voltage pulse shifts the maximum hardness in the direction of a greater value of the constant potential. Submitting $U_{ip} = -2000$ V, maximum hardness falls on $U_b = -150$ V.

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